Tetrahedron Letters,Vol.27,No.25,pp 2809-2812,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

A VERSATILE SYNTHESIS OF VICINAL DIAZIDES USING HYPERVALENT IODINE

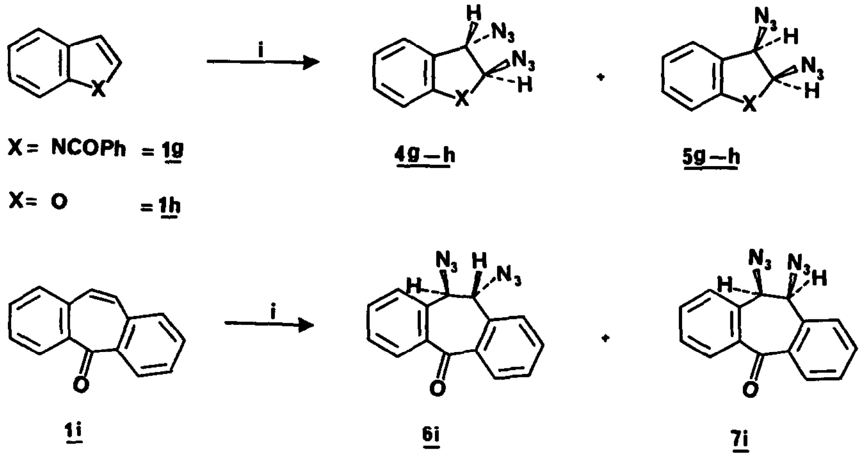
Robert M. Moriarty,* and Jaffar S. Khosrowshahi

Department of Chemistry
University of Illinois at Chicago
Chicago, Illinois 60680

Summary. A convenient synthesis of vicinal diazides from olefins using $C_6H_5IO/HOAc/NaN_3$ is described. A mechanism is proposed which accounts for the stereochemical outcome.

Recently the conversion of alkenes to 1,2-diazides using manganese (III) acetate and sodium azide was reported.[1] This reaction involves presumably a Mn(III)-N_3 complex which carries out a ligand transfer oxidation upon the alkene to yield an azidoalkyl radical which subsequently is attacked by Mn(III)-N_3 to yield the vicinal diazide and Mn(II). 1,2-Diazides are important precursors for the synthesis by reduction[2] of 1,2-diamines which are otherwise difficult to obtain. Hypervalent iodine oxidation of alkenes in the presence of sodium azide offers a simple and high yield route to 1,2-diazides as exemplified in Eqn 1 and Table 1.

$$\underset{\textbf{1a-f}}{RCH{=}CHR'} + NaN_3 + CH_3COOH \xrightarrow{i} \underset{\textbf{2a-f}}{RCH(N_3)CH(N_3)R'} + \underset{\textbf{3 a,e,f}}{RCH(N_3)COR'}$$



i = PhIO/ HOAc/ NaN_3

Table 1

1,2-Diazides from the Hypervalent Iodine Oxidation of Alkenes in the System C_6H_5IO-HOAc-NaN_3[a]

Alkene	Conditions (t°, time hr.)	Vicinal Diazide(%) cis/trans	Azido-ketone(%)
1. trans-stilbene(1a)	50°, 2	2a[b]= (42%) meso:30% dl :70%	$PhCOCH(N_3)Ph$(3a)[b] (14%)
2. cyclohexene(1b)	45°, 3	2b[c]= (40%) cis :15% trans: 85%	
3. styrene(1c)	35°, 3	2c[d]= (70%)	
4. trans-β-methyl styrene(1d)	45°, 2.5	2d= (69%) erythro: 10% threo: 90%	
5. chalcone(1e)	40°, 3.5		$PhCH{=}C(N_3)COPh$(3e)[e] (51%)
6. benzalacetone(1f)	45°, 2.5		$PhCH{=}C(N_3)COCH_3$(3f)[g] (49%)
7. N-benzoylindole(1g)	45°, 3	(34%) 4g:5g[h] =7:2	
8. benzofuran(1h)	R.T.,3	(85%) 4h:5h[i] =7:3	
9. dibenzosuberenone(1i)	35°, 2	(42%) 6i:7i[j] =2:1	

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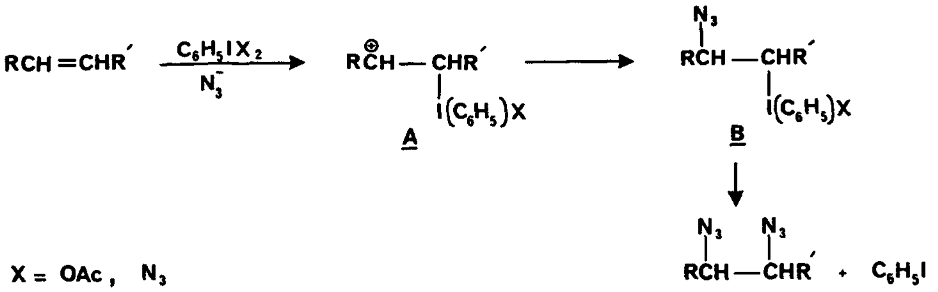
a) General procedure: C_6H_5IO(0.01 mol) in HOAc(25 ml) + alkene (0.01 mol) stirred R.T. 10 min, then NaN_3(0.04 mol) added and the reaction system stirred at indicated temperature and time (behind a safety shield). Work-up: poured into water extd•$CHCl_3$, chromatographed(silica gel 60 mesh), products eluted with benzene, pet-ether 1:1, (b) E. Zbiral and K. Kischa, Tetrahedron Lett., 1167 (1969), (c) G. Emmer and E. Zbiral, Liebigs Ann. Chem., 796, (1979), (d) R. Galli and V. Malatesta, Org. Prep. Proced. Int., 3(5), 231 (1971), (e) G. L'abbe and A. Hassner, J. Org. Chem. 36, 258 (1971), (g) A. Hassner, G. L'abbe and M. J. Miller, J. Am. Chem. Soc. 93, 981 (1971), (h) Y. Tamura, S. Kwon, F. Tabusa, and M. Ikeda, Tetrahedron Lett. 3291 (1975), (i) S. Kwon, T. Okada, M. Ikeda and Y. Tamur, Heterocycles, 6, 33 (1977), N-Benzoylindole (1g) was prepared according to the procedure of Y. Kikugawa, Synthesis, 460 (1981). (j) Higher yield (64%) was obtained when two equivalents of iodosobenzene and eight equivalents of sodium azide were treated with one equivalents of dibenzosuberenone (1i).

Formation of α-azidovinyl ketones 3e and 3f deserves comment. Initial formation of vicinal diazides is assumed in these cases but facile loss of HN_3 occurs due to the driving force for formation of the conjugated carbonyl system.

The pathway which we propose for these reaction involves initial electrophilic attack of the hypervalent iodine species upon the double bond to yield intermediate A. Azide anion may then attack the thus formed carbocation (A→B). Subsequent reductive elimination of iodobenzene with attack by a second azide anion yields the vicinal diazides.



This pathway accounts for the lack of stereoselectivity in the sense that attack of $^-N_3$ upon B may be upon the carbocation (SN_1-like) or via displacement of $I(C_6H_5)X$ (SN_2-like), and the balance between these two pathways will depend upon the nature of the substrate and intermediate A.

The reactions reported here are similar to iodine azide additions.[3] Furthermore, Zbiral and coworkers have studied the functionalization of alkenes with $Pb(IV)(OAc)_4$-$(CH_3)_3SiN_3$[4], $C_6H_5I(III)(OAc)_2$-$(CH_3)_3SiN_3$,[5,7] and $Tl(III)(OAc)_3$-$(CH_3)_3SiN_3$[6].

In the $C_6H_5I(OAc)_2$-$(CH_3)_3SiN_3/CH_2Cl_2$ system oxidative cleavage to a ketonitrile occurs, e.q. α-pinine → cis 1-acetyl-3-cyanomethyl-2,3-dimethylcyclobutane[7], also styrene → ω-azidoacetophenone[7]. By contrast the system C_6H_5IO-HOAc-NaN_3 leads to simple addition of two azido groups in a vicinal arrangement at the original position of the double bond.

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(Received in USA 5 March 1986)